

Enhanced electrochemical performance of sulfur cathode by incorporation of a thin conductive adhesion layer between the current collector and the active material layer

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Abstract A novel coated current collector has been applied to improve the electrochemical performance of sulfur cathode. The conductive adhesion layer was successfully coated onto an Al foil by a simple slurry-coating method, as examined by scanning electron microscopy. The effect of the conductive adhesion layer on the electrochemical performance of sulfur cathode was investigated by charge–discharge cycle tests, cyclic voltammetry (CV) and electrochemical impedance spectroscopy. The results of electrochemical tests demonstrate that introducing conductive adhesion layer not only increases the rate capacity, but also greatly enhances the cycle performance of sulfur cathode with a specific capacity of 497.5 mAh g^{-1} after 50 cycles. The remarkable enhancements can be attributed to the reduction in charge transfer resistance. The curves of CV indicate that the sulfur cathode containing conductive adhesion layer displays an improved electrochemical reversibility.

Keywords Lithium–sulfur battery · Thin conductive adhesion layer · Cyclability · Rate performance

1 Introduction

Lithium–sulfur battery is regarded as the most promising candidate for the next generation batteries due to its high theoretical specific capacity of $1,672 \text{ mAh g}^{-1}$ and theoretical energy density of $2,600 \text{ Wh kg}^{-1}$ [1–4]. In addition, it has advantages of natural abundance, low cost and low toxicity. However, the use of sulfur as cathode material has many problems, such as low utilization of sulfur, rapid capacity fading, which is due to the high solubility of intermediate products (Li_2S_x , $4 \leq x \leq 8$) in commonly used liquid electrolyte [5, 6], the large volume change between sulfur and Li_2S phases [7], especially the electron and ion insulating nature of sulfur [8–11]. One of the effective strategies to enhance electrochemical performance of sulfur electrode is to reduce the overall resistance of the electrochemical system [12, 13].

Many approaches have been proposed to reduce the overall resistance of lithium–sulfur battery. Much attention has been paid to prepare the carbon–sulfur composite materials (mesoporous carbon, carbon spheres, carbon fibers, graphene, carbon nanotubes, and so on) [14–20]. The conductivity of sulfur cathode has been obviously improved. Besides, various cell configuration modifications also have attracted enormous attention. For example, Manthiram and co-workers inserted an interlayer between the sulfur cathode and the separator, such as microporous carbon paper [21], which largely decreased the charge transfer resistance and facilitated the absorption of soluble polysulfides. However, the research on the modification of electrode configuration is still rarely reported.

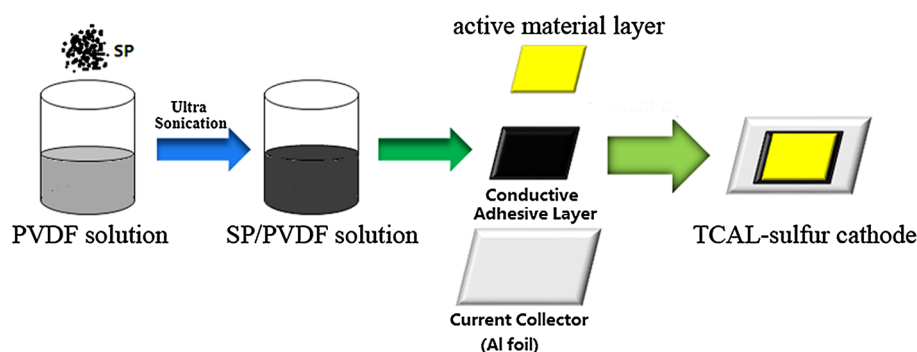
In the typical electrode configuration, the active material layer is directly supported on a metallic current collector. The interface between current collector and active material layer imposes additional charge transfer resistance. For

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Fig. 1 Fabrication procedure for the sulfur cathode containing TCAL



traditional lithium-ion battery, much effort has been devoted to decrease the part of resistance. A conductive adhesive layer containing graphene/PVDF composites was inserted between the Cu current collector and the silicon/graphite layer by Lee [22]. The existence of conductive layer guaranteed high adhesion and good electronic conductivity, which resulted in improved electrochemical performance of the silicon/graphite electrode. Therefore, introduction of conductive adhesive layer between the current collector and the sulfur layer may further promote the electrochemical performance of sulfur cathode.

In this study, we introduced a thin conductive adhesion layer (TCAL) between the aluminum current collector and the active material layer by a simple slurry-coating method, and the electrochemical performance of sulfur cathode was investigated as well. The results show that the existence of conductive adhesion layer could remarkably enhance the electrochemical performance of the sulfur cathode, especially the cycling performance.

2 Experimental

2.1 Preparation of sulfur cathodes containing a thin conductive adhesion layer

Commercial carbon black (Super P Timcal) was added to 8 wt% polyvinylidene fluoride (PVDF 6020 Solef) solution with *N*-methylpyrrolidinone (NMP) as solvent and was ultrasonically dispersed for 1 h. This slurry was coated on aluminum foil (30 μm thickness) and then was dried in a convection oven at 100 $^{\circ}\text{C}$ for 12 h to obtain carbon-coated aluminum foil. The thickness of the conductive adhesion layer was approximately 5 μm .

The sulfur cathodes were prepared by a conventional slurry-coating method with a doctor blade. The cathode slurry was prepared by mixing 60 wt% sublimed sulfur (99.98 %, Aldrich), 30 wt% carbon black (Super P Timcal) and 10 wt% PVDF (6020 Solef). Then, the slurry was spread onto two types of aluminum current collector,

routine aluminum foil and carbon-coated aluminum foil. The electrodes were dried under vacuum at 70 $^{\circ}\text{C}$ for 24 h. The sulfur loading density was 1.6 mg cm^{-2} . For brevity, the sulfur cathodes containing the TCAL will hereafter be referred to as TCAL sulfur cathode, and the sulfur cathodes without the TCAL will be referred to as ordinary sulfur cathode. The coin cells containing these electrodes will adopt the same notation. A schematic illustration of the fabrication of the sulfur cathode containing a thin conduction adhesion layer is shown in Fig. 1.

2.2 Cell assembly and characterization

Coin-type (CR2025) cells were assembled in an argon-filled glove box (Universal 2440/750) in which oxygen and water contents were less than 1 ppm. Sulfur electrode was used as the cathode, lithium foil as the counter and reference electrode, microporous polypropylene membrane as the separator and 1.5 mol L^{-1} lithium bis(trifluoromethane sulfonyl)imide (LiTFSI, 99.95 %, Aldrich) in a solvent mixture of 1,3-dioxolane and 1,2-dimethoxyethane (1:1, v/v) as the electrolyte.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted using Solartron 1470E cell test. The cyclic voltammograms (CV) and the EIS of the working electrode were carried out in three-electrode system, and the sulfur cathode was used as the working electrode, and metallic lithium was used as the reference electrode and the counter electrode. CV tests were performed at a scan rate of 0.2 mV s^{-1} in the potential range of 1.5–3.0 V. AC impedance measurements were carried out at open-circuit potential in the frequency range between 100 kHz and 10 mHz with a perturbation amplitude of 5 mV. The galvanostatic charge/discharge tests were carried out at a constant current density of 335 mA g^{-1} (0.2 C) in the potential range of 1.5–3.0 V under a LAND CT2001A charge–discharge system. All experiments were conducted at room temperature. The morphologies of the current collectors were observed with a scanning electron microscopy (SEM) (FEI Quanta-200).

Fig. 2 SEM image of **a** Al current collector, **b** thin conductive adhesion layer

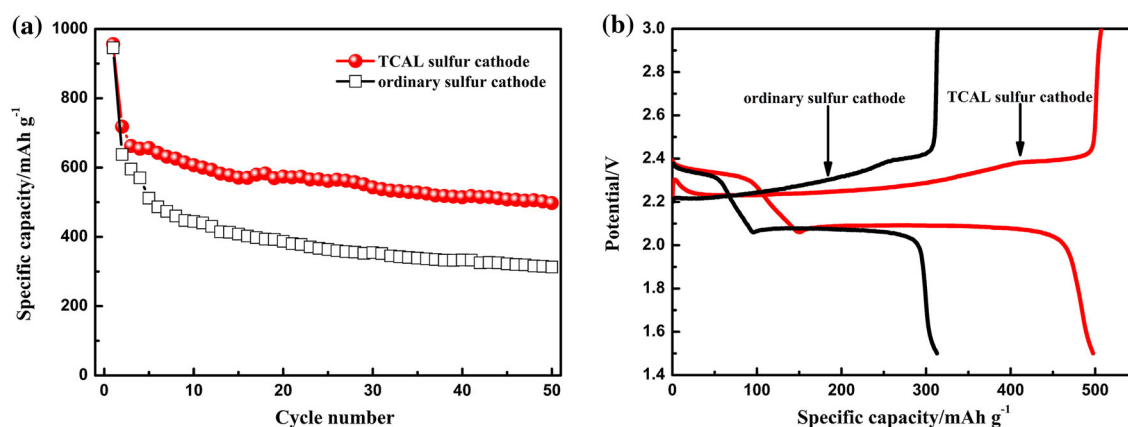
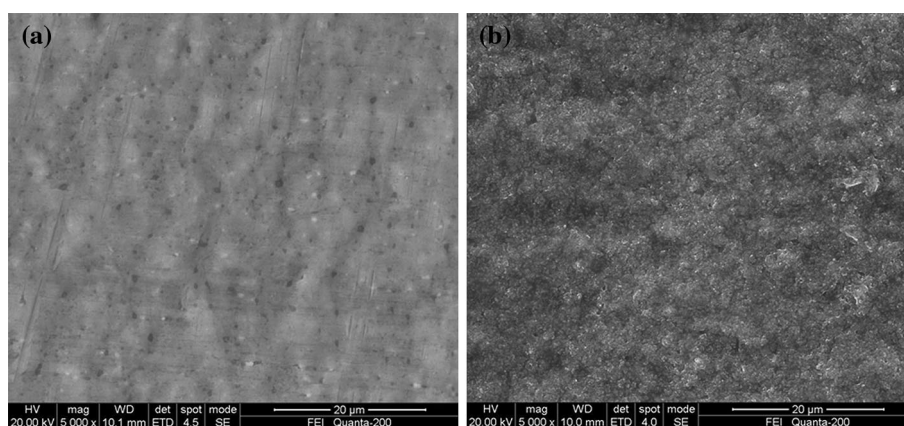


Fig. 3 **a** Cycle performance of the TCAL sulfur cathode and the ordinary sulfur cathode at the current of 335 mA g^{-1} . **b** Discharge/charge curves of the TCAL sulfur cathode and the ordinary sulfur cathode at 335 mA g^{-1} at 50th cycle

3 Results and discussion

3.1 SEM

Figure 2a, b shows the surface morphologies of the aluminum current collector and the TCAL, respectively. As shown in Fig. 2a, b, the obvious morphological difference between the aluminum current collector and the TCAL can be observed. The surface of the conductive adhesion layer is much rougher than that of aluminum current collector. The rough surface of the conductive adhesion layer can improve the contact properties with the sulfur layer. The close contact between the conductive adhesion layer and the sulfur layer can promote rapid electron transmission and reduce the interface charge transfer impedance.

3.2 Charge and discharge performance

Cycling performance of ordinary sulfur cathode and TCAL sulfur cathode between the 1.5 and 3.0 V at a constant current density of 335 mA g^{-1} is present in Fig. 3a. All the capacity value in this study is calculated based on sulfur mass. It can be

seen that the capacity of the ordinary sulfur cathode and the TCAL sulfur cathode is decreased with the increasing number of cycles. As shown in Fig. 3a, the initial discharge capacity of the ordinary sulfur cathode is 945.6 mAh g^{-1} , and it delivers a reversible capacity of 312.9 mAh g^{-1} after 50 cycles, which is similar to the results of Dong [23]. For the TCAL sulfur cathode, it provides the initial capacity of 956.3 mAh g^{-1} and retains 497.5 mAh g^{-1} after 50 cycles, showing a great improvement in cyclability.

Figure 3b shows the 50th cycle charge/discharge curves of Li/S cell with the ordinary sulfur cathode and the TCAL sulfur cathode at the current density of 335 mA g^{-1} . Two typical discharge potential plateaus are observed for both cathodes, corresponding to the multistep of reduction reaction of sulfur during the discharge process, similar to the literature reported by Shin [24]. As shown in Fig. 3b, the TCAL sulfur cathode shows a lower charge plateaus and a higher discharge plateaus than that of ordinary sulfur cathode, which suggests that the TCAL sulfur cathode has smaller electrochemical polarization.

The rate capability of the ordinary sulfur cathode and the TCAL sulfur cathode is shown in Fig. 4. The discharge

capacity of both ordinary sulfur cathode and TCAL sulfur cathode gradually decreases as the current rate increases from 0.2C to 1C. The ordinary sulfur cathode only delivers a specific capacity of 160.7 mAh g⁻¹ at 1 C, similar to the results of Tao [25]. However, for the TCAL sulfur cathode, a satisfactory capacity of 343.5 mAh g⁻¹ can be obtained. Moreover, the TCAL sulfur cathode can recover most of the capacity when the current rate is reduced back to 0.2 C. Such improved rate performance of the TCAL sulfur cathode can be attributed to the reduced interfacial resistance between the sulfur layer and the current collector.

3.3 Cyclic voltammogram

Figure 5 shows the comparison of initial CV curves of Li/S cells with the ordinary sulfur cathode and TCAL sulfur cathode. Both curves indicate two distinct reduction peaks and one oxidation peak. During the first cathodic scan of TCAL sulfur cathode, two pronounced reduction peaks at 2.0 and 2.3 V are observed, which are related to the conversion of element sulfur into soluble lithium polysulfides (Li₂S_n, 4 ≤ n ≤ 8) and the reduction of lithium polysulfides to insoluble Li₂S₂ and Li₂S, respectively. During the subsequent anodic scan process, only one sharp oxidation peak is observed in the potential of 2.45 V, which corresponds to the conversion of Li₂S into high-order polysulfides [26]. By comparing the CV curves of the ordinary sulfur cathode and the TCAL sulfur cathode, it can be seen that the reduction and oxidation peaks of the TCAL sulfur cathode are much sharper than those of the ordinary sulfur cathode. Furthermore, the potential gap (ΔE) between oxidation and reduction peaks for the TCAL sulfur cathode is smaller than that of ordinary sulfur cathode. The results indicate that the TCAL sulfur cathode has better electrochemical reversibility.

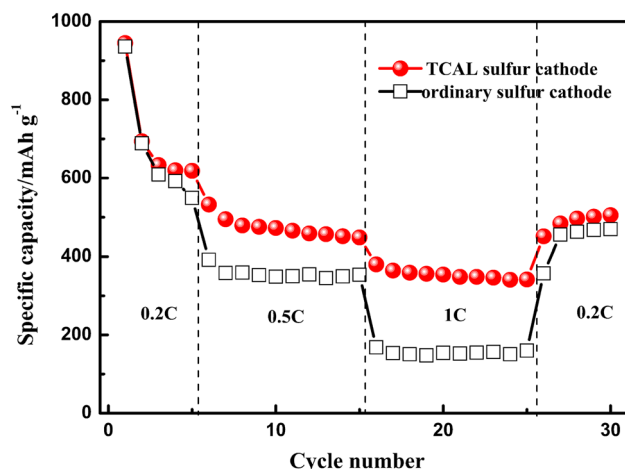


Fig. 4 Rate performance of the TCAL sulfur cathode and ordinary sulfur cathode

3.4 Electrochemical impedance

Electrochemical impedance spectroscopy of fresh cells with the ordinary sulfur cathode and TCAL sulfur cathode are presented in Fig. 6. It can be seen from Fig. 6 that the impedance plots are composed of a depressed semicircle at high frequency and an inclined line in the low frequency region. The width of the semicircle corresponds to the overall charge transfer resistance of the cathode, including bulk impedance and interfacial impedance. In addition, the inclined line at low frequency reflects diffusion of Li ion into the active mass [27]. It is clear that the charge transfer resistance of TCAL sulfur cell is much smaller than that of the ordinary sulfur cell. The observed difference in the charge transfer resistance is apparently associated with the

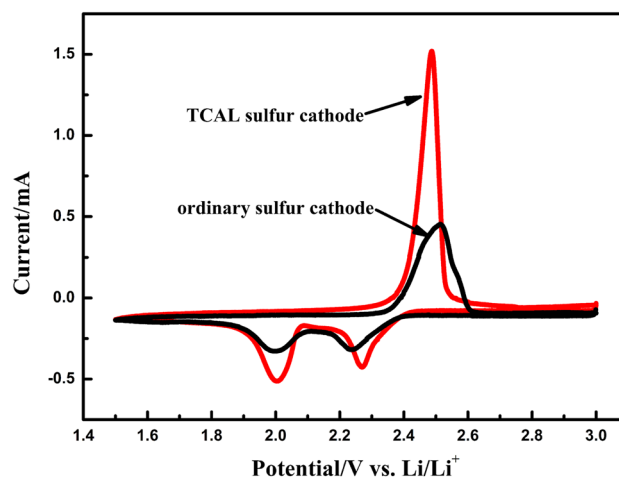


Fig. 5 Cyclic voltammogram curves of the Li/S cells with the TCAL sulfur cathode and the ordinary sulfur cathode at a scan rate of 0.2 mV s⁻¹

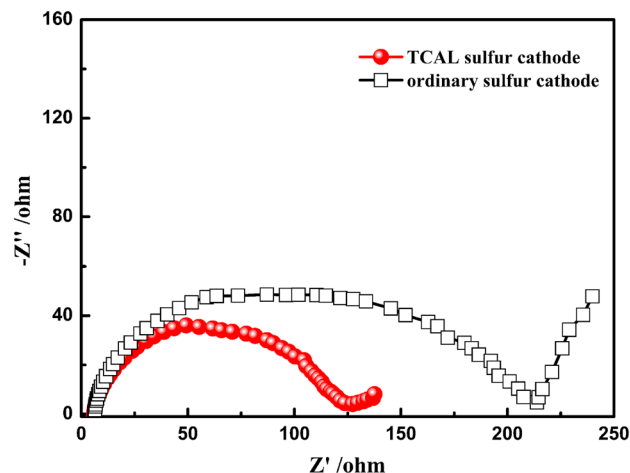


Fig. 6 Nyquist plots for the TCAL sulfur cathode and the ordinary sulfur cathode before cycling

increase in the contact area between sulfur layer and current collector. As a result, the TCAL sulfur cells show better cycle performance and rate performance.

4 Conclusion

In summary, the insertion of the TCAL, through a simple physical slurry-coating method, contributes to the electrochemical performance of sulfur cathode. SEM observation indicates the TCAL has rougher surface, which leads to close adhesion with the sulfur layer. Meanwhile, the result of EIS confirms that the charge transfer resistance of TCAL sulfur cathode is significantly decreased. Compared with the ordinary sulfur cathode, the TCAL sulfur cathode exhibits better reversibility, excellent cycle stability of 497.5 mAh g^{-1} after 50 cycles. Therefore, we believe the work reported here may contribute to the commercial application of Li–S batteries in future.

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